



Project Summary

Field Evaluation (First) of VOST and SemiVOST Methods for Selected CAAA Organic Compounds at a Coal-Fired Power Plant

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Abstract

Laboratory and field studies for volatile organic sampling trains (VOST) and semivolatile organic sampling trains (SemiVOST) have been performed to evaluate the performance of halogenated volatile and semivolatile organic analytes from Title III of the Clean Air Act Amendments (CAAA) of 1990. Laboratory tests were conducted to determine if candidate nonhalogenated CAAA analytes and pesticides could be analyzed by gas chromatography/mass spectrometry (GC/MS). Organic compounds that could not be analyzed successfully were eliminated from further study. Gaseous and liquid dynamic spiking experiments were performed in the laboratory using the candidate sampling trains and the remaining analytes. A method evaluation study was subsequently conducted in the field. Three spiking schemes were employed in the field evaluation study: Volatile organic compounds were spiked into VOST trains as a gaseous spike, and semivolatile organic compounds were spiked into SemiVOST trains as a mixture of either Acid/Neutral compounds or Base/Neutral compounds. These two mixtures were evaluated in separate sampling runs to avoid losses due to known acid/base chemical reactions. This field evaluation study was performed at a clean source with low moisture levels and minimal background levels of organic compounds. Ten quadruple sampling (each) runs were performed for VOST, Acid/Neutral SemiVOST, and Base/Neutral SemiVOST. Each quadruple run used four collocated sampling probes into four similar sam-

pling trains, with two spiked trains and two unspiked trains. Statistical analysis of the results was performed according to the guidelines of EPA Method 301.

This Project Summary was developed by the National Exposure Research Laboratory's Air Measurements Research Division, Research Triangle Park, NC, to announce key findings of the research project that is fully documented in a separate report of the same title (see Project Report ordering information at back).

Introduction

After laboratory and field studies were performed to evaluate the performance of halogenated volatile and semivolatile organic analytes from Title III of the Clean Air Act Amendments (CAAA) of 1990 in VOST and SemiVOST methodology, nonhalogenated CAAA organic analytes and pesticides were similarly evaluated. Laboratory studies were performed to determine if candidate analytes could be analyzed by GC/MS because both VOST and SemiVOST require GC/MS analysis. The analytical methodology used for the VOST was SW-846 Method 5041; SW-846 Method 8270 was used for the SemiVOST.

When the 19 nonhalogenated candidate VOST analytes from the CAAA list were spiked onto VOST tubes and analyzed by thermal desorption/purge and trap/GC/MS, candidate VOST analytes with poor analytical response were eliminated from further testing. The five remaining candidate VOST analytes were supplied in a certified gas cylinder by a commercial vendor for use in laboratory and field dynamic spiking experiments.

The semivolatile nonhalogenated organic compounds and pesticides selected from the CAAA list were combined into multi-component solutions and the solutions were analyzed by GC/MS according to the procedures of EPA Method 8270. Several different combinations of analytes were analyzed, and several analytes were eliminated from further testing because of chemical incompatibilities in solution and lack of solubility in methylene chloride at the levels desired for a spiking solution. Semivolatile organic analytes were ultimately combined into three individual solutions: Acid, Base, and Neutral. Methylene chloride solutions of combined Acid and Neutral compounds or Base and Neutral compounds were prepared for use in SemiVOST evaluation procedures.

Laboratory dynamic spiking studies were performed to evaluate VOST and SemiVOST method precision and bias under controlled conditions. Laboratory sampling conditions included clean laboratory air sampled with dual VOST or SemiVOST trains. The results of the laboratory dynamic spiking studies were used to predict the behavior of the volatile and semivolatile organic compounds under field test conditions, with results from the preliminary laboratory study used to direct the spiking strategy for the first field test.

Procedure

A coal-fired power plant that does not routinely emit high levels of the hazardous air pollutants (HAPs) was selected as a test site for a field evaluation of the VOST and SemiVOST methods applied to nonhalogenated volatile and semivolatile organic compounds. The absence of high levels of volatile and semivolatile organic compounds in the background matrix of the stationary source was established during a pretest survey. Field testing was conducted to assess the effect of sampling a combustion matrix (stack gas).

Field evaluation of both VOST and SemiVOST was accomplished by sampling and analysis following the EPA methods (VOST: sampling, EPA Method 0030; analysis, EPA Method 5041; SemiVOST: sampling, EPA Method 0010; sample preparation, EPA Proposed Method 3542; analysis, EPA Method 8270) except for the use of four collocated sampling probes (Quad probe). This modification of the sampling trains was necessary to conform to the requirements of EPA Method 301 for determining the bias and precision of test methods. EPA methods were applied exactly as written, with no deviation from the written methodology.

Generation of data for the validation of test methodology according to EPA

Method 301 allows the bias (systematic error) and precision (reproducibility of measurement) to be determined in a statistically valid manner.

To determine bias and precision in the field, ten quad sampling runs (40 sampling trains) were performed for each of the VOST, Acid/Neutral SemiVOST, and Base/Neutral SemiVOST. The additional quadruple runs were performed in the field to allow for possible loss of samples or invalidation of a run for any reason.

Analytical Results

Laboratory studies using GC/MS demonstrated that 5 of 19 volatile organic compounds could be used for field testing. The volatile organic compounds that were not tested included acetonitrile, acrylonitrile, 1,1-dimethylhydrazine, 1,4-dioxane, ethyl acrylate, ethylene imine, methyl ethyl ketone, methyl isobutyl ketone, methyl methacrylate, methyl *tert*-butyl ether, propylene oxide, 1,2-propylene imine, triethylamine, and vinyl acetate. The semivolatile organic compounds that were not tested in the field included hydroquinone, 1,4-phenylenediamine, captan, 1,3-propane sultone, ethylene thiourea, hexamethylene-1,6-diisocyanate, maleic anhydride, quinone, catechol, and 2,4-toluenediamine.

Analytical field data were evaluated according to the statistical procedures of EPA Method 301, and according to the criteria of the EPA Handbook for Quality Assurance/Quality Control (QA/QC) Procedures for Hazardous Waste Incineration (EPA/625/6-89/023, January, 1990). The compounds tested in the field study are listed in Table 1. Their recoveries and whether they meet the criteria of the two statistical procedures are also shown in Table 1.

Discussion

Based on the work performed in the laboratory and the field evaluation of the VOST and SemiVOST method for nonhalogenated analytes and pesticides listed in Title III of the Clean Air Act Amendments of 1990, the following observations may be made:

- Where the test atmosphere is clean dry laboratory air, performance in laboratory testing is a reasonably reliable indicator of field performance. However, there are a few examples where marginal performance in the laboratory precedes acceptable field performance as well as several instances where good laboratory performance precedes unacceptable field performance.
- The two modes of statistical calculation (EPA Method 301 and EPA QA Handbook) generally produce comparable results. An analyte which

meets one set of acceptance criteria usually meets the other set of acceptance criteria as well, or the analyte will fail to meet both sets of criteria. An exception to this observation occurs when the Method 301 correction factor is in the range of 1.30 to approximately 2.00: Analytes with a Method 301 correction factor in this range meet QA Handbook acceptance criteria although the Method 301 correction factor is not acceptable. An analyte with a Method 301 correction factor lower than 0.70 can also meet EPA Handbook acceptance criteria.

- Several of the nonhalogenated organic analytes demonstrated solubility problems in the course of preparation of a stock solution in methylene chloride. These analytes are not appropriate for the SemiVOST methodology because quantitative extraction by methylene chloride cannot be ensured. The utility of SemiVOST even as a screening method for the presence of these analytes is questionable.
- Reactive nonhalogenated semivolatile organic analytes which demonstrated reaction with other components of the stock or spiking solution are questionable as appropriate for the SemiVOST method because the extent of reaction cannot be determined; therefore, the accuracy of the quantitative values is suspect. The utility of SemiVOST even as a screening method for the presence of these analytes is questionable.
- The VOST is appropriate as a sampling/analytical method only for those CAAA volatile organic analytes which can be analyzed by GC/MS. The VOST is not appropriate even as a screening method for those volatile organic compounds which cannot be analyzed at all by the methodology.
- Quantitative analysis of very polar semivolatile compounds is difficult with the SemiVOST method.
- The presence of particulate matter in the SemiVOST method causes retention of significant amounts of polar semivolatile organic analytes on the filter. Even relatively volatile polar analytes such as aniline are retained on the heated filter of the sampling train. Significant retention of relatively volatile polar analytes on the filter appears to occur for nitrogen-containing analytes such as aniline or quinoline; relatively volatile oxygenated analytes such as phenol do not appear to be retained on the filter.

Table 1. Experimental Results Summary

Analyte	Percent Recovery \pm RSD	Meets Method 301 Criteria in Field? ¹	Meets QA Handbook Criteria in Field? ²
VOST Analytes			
benzene	106 \pm 25.6	Yes	Yes
carbon disulfide	63.1 \pm 18.3	No; correction factor 1.47	Yes
n-hexane	79.2 \pm 22.6	Yes	Yes
toluene	77.9 \pm 17.5	Yes	Yes
2,2,4-trimethylpentane	63.1 \pm 18.3	No; correction factor 1.48	Yes
SemiVOST Analytes			
acetophenone	96 \pm 12	Yes	Yes
4-aminobiphenyl	50 \pm 41	Yes	Yes
aniline	70 \pm 24	No; correction factor 1.37	Yes
o-anisidine	39 \pm 39	No; correction factor 2.53	No; recovery 39.4%
benzidine	65 \pm 119	No	No
biphenyl	103 \pm 12	Yes	Yes
bis(2-ethylhexyl) phthalate	48 \pm 23	No; correction factor 2.16	No; recovery 48%
cumene	88 \pm 11	Yes	Yes
dibenzofuran	100 \pm 12	Yes	Yes
di-n-butyl phthalate	46 \pm 54	No; correction factor 2.44	No; recovery 46%
N,N-diethylaniline	95 \pm 19	Yes	Yes
N,N-dimethylaniline	67 \pm 24	No; correction factor 1.42	Yes
dimethylaminoazobenzene	31 \pm 51	No; correction factor 3.26	No
3,3'-dimethoxybenzidine	37 \pm 38	No	No
dimethyl phthalate	82 \pm 17	No; correction factor 1.31	Yes
4,6-dinitro-o-cresol	122 \pm 14	Yes	Yes
2,4-dinitrophenol	111 \pm 31	Yes	Yes
2,4-dinitrotoluene	109 \pm 12	Yes	Yes
3,3'-dimethylbenzidine	92 \pm 44	Yes	Yes
isophorone	93 \pm 12	Yes	Yes
4,4'-methylene	89 \pm 36	Yes	Yes
4,4'-methylene bis(chloroaniline)	89 \pm 36	Yes	Yes
4,4'-methylenedianiline	6 \pm 73	No	No
o-cresol	90 \pm 15	Yes	Yes
m-/p-cresol ³	69 \pm 14	No; correction factor 1.51	Yes

¹Acceptance criteria: correction factor between 0.70 and 1.30, precision $\leq 50\%$ relative standard deviation.

(continued)

²Acceptance criteria: recovery between 50% and 150%, precision $\leq 50\%$ relative standard deviation.³These compounds are listed together in the table because the coelute and are not separated in analysis.

Table 1. Continued

Analyte	Percent Recovery \pm RSD	Meets Method 301 Criteria in Field? ¹	Meets QA Handbook Criteria in Field? ²
naphthalene	96 \pm 11	Yes	Yes
nitrobenzene	109 \pm 12	Yes	Yes
4-nitrobiphenyl	102 \pm 14	Yes	Yes
4-nitrophenol	114 \pm 31	Yes	Yes
N-nitrosodimethylamine	117 \pm 13	Yes	Yes
N-nitrosomorpholine	116 \pm 12	Yes	Yes
phenol	89 \pm 8	Yes	Yes
o-toluidine	56 \pm 30	No; correction factor 1.77	Yes
trifluralin	27 \pm 41	No; correction factor 3.81	No
ethylbenzene	89 \pm 12	Yes	Yes
styrene	84 \pm 10	Yes	Yes
o-xylene	85 \pm 11	Yes	Yes
m-/p-xylene ³	79 \pm 12	Yes	Yes
2-acetylaminofluorene	147 \pm 23	No; correction factor 0.68	Yes
caprolactam	114 \pm 12	Yes	Yes
carbaryl	99 \pm 14	Yes	Yes
chlordane	142 \pm 16	Yes	Yes
DDE	102 \pm 15	Yes	Yes
dichlorvos	101 \pm 18	Yes	Yes
heptachlor	103 \pm 12	Yes	Yes
hexamethylphosphoramide	14 \pm 118	No; correction factor 6.93	No
lindane	104 \pm 12	Yes	Yes
methoxychlor	73 \pm 19	No; correction factor 1.40	Yes
parathion	89 \pm 28	No; correction factor 1.31	Yes
propoxur	123 \pm 12	Yes	Yes
quinoline	80 \pm 19	Yes	Yes
styrene oxide	0.5 \pm 1481	No	No
1,4-dioxane	87 \pm 11	Yes	Yes
ethyl carbamate	103 \pm 14	Yes	Yes
methyl isobutyl ketone	112 \pm 11	Yes	Yes
phthalic anhydride	5.3 \pm 144	No	No

¹Acceptance criteria: correction factor between 0.70 and 1.30, precision $\leq 50\%$ relative standard deviation.

²Acceptance criteria: recovery between 50% and 150%, precision $\leq 50\%$ relative standard deviation.

³These compounds are listed together in the table because they coelute and are not separated in analysis.

- The least volatile semivolatile organic analytes are distributed mostly on the heated filter of the sampling train. For some types of particulate matter, it may not be possible to recover organic analytes quantitatively using methylene chloride extraction techniques.
- Analytes tested using both VOST and SemiVOST include 1,4-dioxane and methyl isobutyl ketone. For these two polar volatile organic analytes, VOST was unsuccessful; SemiVOST was successful.

Conclusions and Recommendations

Successful operation of the SemiVOST methodology, including validation, depends on several considerations which can be evaluated only by testing the operation of the entire methodology:

- The chemical nature of the compounds of interest must be considered. EPA Method 0010 states that the range of applicability is all organic compounds with a boiling point above 100°C. This statement provides only a general guideline that excludes organic compounds with a boiling point below 100°C. The statement does not guarantee that any organic compound in the appropriate boiling point range will function successfully in the SemiVOST methodology. Polar compounds are more reactive, more difficult to extract, and more difficult to analyze than non-polar compounds. Any of these factors may make it impossible to sample or analyze the compound using the SemiVOST methodology.
- The nature of the background stationary source matrix is an important consideration in determining the successful function of the SemiVOST method. Highly acidic stationary source matrices affect compound recoveries. Extremely wet source matrices introduce difficulties in sample extraction. High levels of particulate material can retain organic compounds. All of these factors of the stationary source demonstrate why successful laboratory performance of a given compound cannot guarantee that the compound will perform successfully in the field. However, inability to analyze the compound by GC/MS in the laboratory does guarantee that performance of the sampling and analytical methodology cannot even be evaluated.
- Neutral, non-polar compounds as a class tend to demonstrate the best performance in the SemiVOST methodol-

ogy. Acidic or basic compounds are reactive. These compounds tend to react with each other or with constituents of the source matrix, thus limiting or eliminating their recovery using the SemiVOST method.

The successful performance of the VOST method also demands evaluation of the entire sampling and analytical method:

- The chemical nature of the compounds of interest must be considered. EPA Method 0030 states that the range of applicability is all organic compounds with a boiling point below 100°C. This statement provides only a general guideline that excludes organic compounds with a boiling point above 100°C, although in practical application of the method this boiling point limitation is frequently extended to 132°C. The statement does not guarantee that any organic compound in the appropriate boiling point range will function successfully in the VOST methodology. Polar compounds are more reactive, more difficult to desorb and purge, and more difficult to analyze than non-polar compounds. Any of these factors may make it impossible to sample or analyze the compound using the VOST methodology.
- The nature of the background stationary source matrix is an important consideration in determining the successful function of the VOST method. Highly acidic stationary source matrices affect compound recoveries. Extremely wet source matrices introduce difficulties in sample desorption. Reactive constituents of the source matrix can react with the sorbent or the sorbed compounds. All of these factors of the stationary source demonstrate why successful laboratory performance of a given compound cannot guarantee that the compound will perform successfully in the field. However, inability to analyze the compound by GC/MS in the laboratory does guarantee that performance of the sampling and analytical methodology cannot even be evaluated.
- Neutral, non-polar compounds as a class tend to demonstrate the best performance in the VOST methodology. Acidic or basic compounds are reactive. These compounds tend to react with each other or with constituents of the source matrix, thus limiting or eliminating their recovery using the VOST method.

On the basis of the laboratory and field effort conducted thus far for the nonha-

logenated volatile and semivolatile organic analytes listed in Title III of the Clean Air Act Amendments of 1990, the following recommendations are made:

- Faced with a candidate analyte for either VOST or SemiVOST for which no method validation information is available, laboratory experimentation can aid in establishing the validity of assigning the analyte to a particular methodology.
- Careful consideration of the chemical properties (acid, base, reactivity, etc.) of candidate analytes is essential in predicting success or failure in the application of VOST or SemiVOST sampling and analytical methodology.
- A complete and accurate formulation of the complete SemiVOST methodology as it is presently used should be written. Method 0010 is applicable for sampling procedures but sample preparation procedures contained in Method 0010 have been superseded by Proposed Method 3542. The complete Method 8270 is not applicable as the analytical methodology; only certain sections are applicable. Also, Method 8270 surrogate compounds are usually used with SemiVOST samples.
- Further study of the VOST analytical methodology (Method 5041) should be performed. Internal standards and surrogate compounds used in Method 8240 have been used in Method 5041 for the sake of consistency between the methods. However, p-bromofluorobenzene is not an appropriate surrogate compound for the VOST methodology since the boiling point for this compound is 150°C, well above the upper limit of 100°C. A better choice of surrogate compound should be made. Also, no criteria are available in the method for acceptability of surrogate recoveries in the VOST beyond the general guidelines of the QA Handbook of recovery between 50 and 150%, with precision of 50% relative standard deviation.

Disclaimer

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The complete report, entitled "Field Evaluation (First) of VOST and SemiVOST Methods for Selected CAAA Organic Compounds at a Coal-Fired Power Plant," (Order No. PB97-196117; Cost: \$67.00, subject to change) will be available only from:

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